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(54) **Low phosphorus/low zinc lubricants.**

(57) Lubricants having antiwear, corrosion inhibition and antioxidant performance appropriate to modern oil requirements with reduced or zero amounts of zinc and phosphorous and without the need for large amounts and/or expensive forms of antioxidant comprise 5 to 500 parts per million by weight (ppm) of added copper present in oil-soluble form, one or more added oil-soluble sulphur-containing compounds and a bearing corrosion inhibitor.

EP 0 280 579 A2

Description

Low Phosphorus/Low Zinc Lubricants

The present invention relates to lubricating compositions, especially automobile crankcase lubricants, containing low or zero amounts of phosphorus and zinc.

There is currently a drive to reduce the amounts of phosphorus in lubricants because of the deleterious effect phosphorus has on catalysts commonly used in catalytic converters used for emission control. Levels of phosphorus have typically been of the order of 0.1% but there is an increasing need to reduce phosphorus levels to below 0.05 wt % or remove it altogether. However, zinc dialkyl dithiophosphates (ZDDP) and other phosphorus containing additives have been widely used as anti-wear and/or anti-oxidant additives and simply reducing or removing such components results in lubricants with poor engine performance.

This invention provides lubricant compositions and concentrates with low or zero amounts of phosphorus and zinc, and which comprise copper, sulphur, and a bearing corrosion inhibitor, which compositions have been found to have remarkable engine performance.

US-A-2356661 deals with lubricating oils containing 50 to 1000 parts per million of copper as an oil-soluble organic compound such as copper dialkyl dithiocarbamates and including phosphorus containing compounds together with from 0.1 to 0.5 wt % of total sulphur in the oil, sulphur being provided as oil-soluble organic sulphur compounds such as thiocarbamates.

US-A-2343756 discloses the addition of copper compounds including phosphorus-containing copper complexes in conjunction with sulphur compounds, to lubricating oils. Amounts of from 0.1 to 0.5 wt % of sulphur are disclosed, with amounts in excess of 0.5 wt % sulphur described as being potentially detrimental. In US-A-2552580, cuprous thiophosphates are included in lubricant compositions at relatively high levels, which will give high phosphorus level in the oils. In US-A-3346493, a wide variety of metal-containing polymeric amine-metal reactants are employed as detergents in lubricant compositions. In an isolated example, a lubricant is described containing inter alia, a copper salt of an acylated nitrogen compound, 0.075% phosphorus as a ZDDP reacted with hexene oxide, and a sulphurized methyl ester of a tall oil acid. Other copper containing lubricants either contain more phosphorus or no sulphur. US-A-4122033 discloses the entire group of transition metal compounds as antioxidation stabilizers in conjunction with amines, selenides, phosphines or phosphites and may be used in various applications including as additives for lubricants. None of the foregoing documents describe fully formulated lubricant oils which would be appropriate to meet the requirements for modern lubricants and none specifically address the reduction of phosphorus levels while maintaining performance in antiwear, antioxidation and corrosion inhibition.

EP-A-24146 discloses lubricant compositions containing an ashless dispersant and/or polymeric viscosity index improver dispersant and copper which may be in the form of a dithiocarbamate, but requires the presence of from 0.01 to 0.5 wt% zinc and from 0.01 to 0.5 wt % phosphorus. Thiadiazole polysulphides are an optional component.

US-A-4330420 describes oils with reduced phosphorus content (but only to 0.05%P) using mixtures of dialkyldiphenylamine and a sulphurized polyolefin to compensate for reduction in the amount of ZDDP. There is no disclosure of the use of copper or thiadiazole polysulphides.

EP-A-89844 describes reaction products of 4,4′-methylene-(2,6-di-t-butyl phenol) and tri-Sec-C_{4-12} alkyl orthoborate and their use in lubricants to enable the amount of ZDDP to be reduced to provide from 0.05 to 0.11 wt % P.

US-A-4490265 describes lubricating oils comprising boron-containing heterocyclic compounds which may be in the form of a metal salt including a copper salt, thiadiazole polysulphides, terephthalic acid and as an oxidation inhibitor either a bis(dithiobenzil) metal derivative where the metal may inter alia be copper or a sulphur-bridged, bis hindered phenol. The desirability of reducing or eliminating phosphorus is not disclosed and all the Examples of lubricants contain 0.05 wt% P. US-A-4623474 contains a similar disclosure. US-A-4627930 also describes boron-containing heterocyclic compounds which may be in the form of a copper salt and may be sulphurized. Thiadiazole polysulphides and copper carboxylates are also disclosed. Although the boron-containing heterocyclic compounds are described as phosphorus-free, there is no disclosure of a fully formulated oil containing less than 0.05 wt % P. US-A-4629580 contains a similar disclosure. US-A-4629579 discloses boron and metal-boron derivatives for use as extrement pressure, anti-wear and friction reducing additives for lubricating oils and compositions including one containing no ZDDP, but there is disclosure of a composition containing low or zero amounts of phosphorus, with sulphur and copper.

Lubricant compositions containing low, or zero amounts of phosphorus, but no copper are described in WO-A-8604601, WO-A-8604602 and WO-A-8606092.

The invention seeks to provide lubricants having antiwear, corrosion inhibition and antioxidant performance appropriate to modern oil requirements with reduced or zero amounts of zinc and phosphorus and without the need for large amounts and/or expensive forms of antioxidant.

The term "modern oil" as used herein in relation to automobile crankcase lubricants refers to oil which can meet the current requirements for crankcase lubricants in the major industrial countries. High performance engines, increased lifetime requirements resulting from longer periods between oil changes and higher operating temperatures all contribute to the increased performance required from lubricants. This invention is particularly concerned with automobile lubricants which can meet and exceed the requirements for the SF API

Engine Service Category for service station oils and/or the CD requirements for the CD/API Engine Service Category for Commercial Oils (Diesel Engines) established jointly by API, SAE and ASTM.

In one aspect, this invention provides a lubricant composition comprising a major amount of a lubricating oil, 5 to 500 parts per million by weight (ppm) of added copper present in oil-soluble form, one or more added oil-soluble sulphur-containing compounds such that the composition preferably comprises from greater than 0.5 to 2.0 wt % of total sulphur, more preferably 0.5 to 1.0 wt % of total sulphur, and an effective amount of a bearing corrosion inhibitor, the composition containing less than 0.05 wt % phosphorus and less than 0.01 wt% zinc, preferably being substantially phosphorus-free and zinc-free.

In particularly preferred embodiments of the invention, the lubricant composition will also contain one or more ashless dispersants and/or one or more viscosity index improver dispersants and/or one or more overbased additives which function as antacid and anti-rust agents, such as overbased calcium or magnesium sulphonates or phenates.

The use of copper in the invention enables a low phosphorus oil with performance meeting the requirements for modern oils to be obtained economically and with good control of oxidation, which in an automobile engine is catalysed by metal accumulated in the oil by wear or corrosion, with iron being a particular oxidation catalyst. At unduly low concentrations of copper, the anti-oxidant effect may not be sufficient for some applications. At unduly high concentrations the ash level of the oil will be increased and an increased tendency to bearing corrosion may be observed. The amount of added copper in the compositions will generally be within the range of 10 to 400 ppm, typically 10 to 300 ppm, preferably 10 to 200 ppm, e.g. 60 to 200 ppm.

The ability of the compositions of the invention comprising low amounts of oil-soluble copper compounds and very low or zero amounts of phosphorus to provide adequate antioxidant and antiwear performance for the stringent requirements of modern engine tests is surprising. Copper is known to act in many situations as an oxidation promoter or catalyst, and closely related metals, such as cobalt and chromium, are not effective lubricant anti-oxidants. EP-A-24146 teaches the presence of at least 0.01 wt % of each of phosphorus and zinc.

It is also surprising that the copper compound functions effectively in compositions which may contain zinc and other metal compounds, such as calcium or magnesium overbased additives, which have an inherent pro-oxidant activity.

The copper compounds used as anti-oxidants in this invention may be chosen from those described in EP-A-24146 as suitable for lubricants provided that the copper compounds are substantially free of phosphorus.

Thus, the copper may be blended into the oil as the oil soluble copper salt of a synthetic or natural carboxylic acid. Examples of suitable carboxylic acids include C_{10} to C_{18} fatty acids such as stearic or palmitic acid, unsaturated acids such as oleic acid, branched carboxylic acids such as naphthenic acids of molecular weight from 200 to 500, neodecanoic or 2-ethylhexanoic acid and alkyl or alkenyl substituted dicarboxylic acids such as polyalkene substituted succinic acids, e.g. octadecenyl succinic acids, dodecenyl succinic acids and polyisobutenyl succinic acids.

The copper may be blended into the oil as oil-soluble copper dithiocarbamates of the general formula $(RR'NCSS)_nCu$, where n is 1 or 2 and R and R' are the same or different hydrocarbyl radicals containing 1 to 18, preferably 2 to 12 carbon atoms such as alkyl, alkenyl, aryl, aralkyl, alkaryl and cycloalkyl radicals. Other copper and sulphur containing compounds such as copper mercaptides, disulphides and thioxanthates are suitable for use in the invention. Copper sulphonates, phenates, and acetylacetonates may also be used.

Alternatively the copper may be introduced in the oil in an oil-insoluble form provided that in the finished lubricant composition the copper is in the form on an oil-soluble compound. The term "added copper" is intended to exclude copper present in the oil as a result of accumulation of copper in the oil during use, e.g. by wear or corrosion of copper-containing components.

The lubricant compositions of the invention contain an added oil-soluble sulphur compound. One preferred class of such sulphur compounds are the dithiocarbamates, preferably of the formula: $(RR'NCSS)_n M$, wherein R, R' and n are as defined hereinbefore and M is a suitable metal such as molybdenum or (as indicated above) copper or a optionally substituted hydrocarbyl radical. Preferred dithiocarbamates are dialkyl dithiocarbamates preferably containing 2 to 12 carbon atoms such as diamyl dithiocarbamates.

Sulphur may also be introduced as a mercaptide particularly the mercaptides of aliphatic mercaptans (including copper mercaptides as indicated above), sulphurized unsaturated organic compounds including sulphurized olefins (e.g. US-A-4119549, US-A-4119550, US-A-4191659 and US-A-4147640), sulphurized Diels-Alder adducts (e.g. US-A-3632566, US-A-3498915 and US-E-27331) and particularly sulphurized unsaturated alcohols and esters such as sperm oil substitutes, sulphides including di- and polysulphides, thioethers, thiophenols, thioxanthates (including copper thioxanthates as indicated above), sulphurized esters, thioesters, thioamides, thiazoles such as benzothiazoles, and particularly mercaptobenzothiazoles, and thiadiazoles.

Mineral lubricating oils contain sulphur, whereas synthetic oils may be sulphur-free, so that the amount of sulphur added as a sulphur-containing compound varies according to the basestock and the sulphur contents of other components in the lubricating composition, more preferably so as to give a sulphur content of greater than 0.5 to 1.0 wt % total sulphur. The lubricant compositions of the invention advantageously contain from 0.5 to 0.7 wt % total S, and most preferably 0.1 to 0.5 wt % S as added oil-soluble sulphur-containing compound preferably in the form of a sulphurized ester.

The bearing corrosion inhibitor is a corrosion inhibitor effective at inhibiting corrosion effects on bearings such as Cu/Pb bearings, where effects such as copper staining and high weight loss can be encountered. Such additives have been found to promote the anti-wear performance of the oil. Preferred bearing corrosion inhibitors are borate esters such as $B(OR)_3$, $(RO)_2B\text{-}O\text{-}B(OR)_2$ or $(ROBO)_3$, $(RO)_2BOR^1OB(OR)_2$ and mixtures (wherein R is a substituted or unsubstituted alkyl, aryl or aralkyl group or two groups R together form a substituted or unsubstituted alkylene group and R^1 is a substituted or unsubstituted alkylene group) and these materials may be derived, for example, from alcohols such as alkoxyalkanols (both short chain alkanols and longer chain alcohols as in US-A-4440656) and polyetheralkanols; mono-,di- and trihydroxy alkanls, e.g. 2-ethylhexanol, 2-ethylhexan-1,3-diol, butane-1,2-diol, butane-1,3-diol glycerol and the acyclic polyols of US-A-2866811; hydroxy esters such as glyceryl mono-oleate; oxazolines derived for example from oleic acid and tris(hydroxymethyl)-amimomethane; sulphur-containing alcohols such as may be obtained by reacting epoxides with mercaptans e.g. t-dodecyl-mercaptoethanol; amino alcohols such as alkanolamines e.g. triethanolamine and tri-isopropanolamine, hydroxyamines made by reacting a primary amine (e.g. oleylamine) or secondary amine with ethylene or propylene oxide and the compounds of US-A-4406802. Preferred alcohols are 2-methylpentan-1,3-diol, butane-1,2-diol, butane-1,3-diol and similar 1,2 and 1,3 diols, and ethoxyethanol.

In a preferred aspect the invention contains from 0.01 to 10 wt %, preferably 0.1 to 5 wt %, of a borate ester especially an ester of an alkoxyalkanol or a polyetheralkanol, e.g. a tris(ethoxyethyl) orthoborate ester or metaborate ester, or a biborate of a diol such as butane-1,3-diol.

As an alternative, the bearing corrosion inhibitor is a thiadiazole mercaptan, especially a thiadiazole polysulphide containing from 5 to 50 carbon atoms, a derivative or polymer thereof. Preferred materials are the derivatives of 1,3,4 thiadiazole polysulphides such as those described in US-A-2719125, 2719126 and 3087932. Especially preferred is the compound 2,5-bis (t-octadithio)-1,3,4-thiadiazole commercially available as Amoco 150 or 2,5-bis(nonyldithio)-1, 3,4-thiadiazole available as Amoco 158. Other similar materials also suitable are described in US-A-3821236, 3904537, 4097387, 4107059, 4136043, 4188299 and 4193882. Derivatives of thiadiazole mercaptans may be used such as esters, condensation products with halogenated carboxylic acids, reaction products with aldehydes and amines, alcohols or mercaptans, amine salts, dithiocarbamates, reaction products with ashless dispersants (e.g. US-A-4140643 and US-A-4136043) and reaction products with sulphur halides and olefins.

These materials are preferably present in an amount of from 0.01 to 10 wt %, more preferably 0.1 to 5.0 wt % of the lubricant composition.

The lubricating compositions may comprise small amounts of phosphorus, less than 0.05 wt %, preferably less than 0.01 wt%, more preferably less than 0.005 wt %, but more preferably the lubricating compositions are substantially free of phosphorus.

In a preferred aspect the lubricating composition further comprises:

(A) from 1 to 10 wt % of an ashless dispersant compound which is:

an ashless nitrogen or ester containing dispersant compound preferably selected from:

(i) oil soluble salts, amides, imides, oxazolines and esters, or mixtures thereof, of long chain hydrocarbon substituted mono and dicarboxylic acids or their anhydrides;

(ii) long chain aliphatic hydrocarbon having a polyamine attached directly thereto; and

(iii) Mannich condensation products formed by condensing a molar proportion of long chain hydrocarbon substituted phenol with 1 to 2.5 moles of formaldehyde and 0.5 to 2 moles of polyalkylene polyamine; wherein said long chain hydrocarbon group is a polymer of a C_2 to C_5 monoolefin, said polymer having a molecular weight of 700 to 5000; and/or

(B) from 0.3 to 10 wt %, of a nitrogen or ester containing polymeric viscosity index improver dispersant which may include

(a) polymers comprised of C_4 to C_{24} unsaturated esters of vinyl alcohol or C_3 to C_{10} unsaturated mono- or di-carboxylic acid with unsaturated nitrogen containing monomers having 4 to 20 carbons;

(b) polymers of C_2 to C_{20} olefin with unsaturated C_3 to C_{10} mono- or di-carboxylic acid neutralised with amine, hydroxy amine or alcohols; and

(c) polymers of ethylene with a C_3 to C_{20} olefin further reacted either by grafting C_4 to C_{20} unsaturated nitrogen containing monomers thereon or by grafting an unsaturated acid onto the polymer backbone and then reacting said carboxylic acid groups with amine, hydroxy amine or alcohol.

The nitrogen containing dispersant additives are those known in the art as sludge dispersants for crankcase motor oils, e.g. such as shown in US-A-3275554, US-A-3565804, US-A-3442808, US-A-3442808, GB-A-983040 or BE-A-658236.

The most commonly used dispersants are those formed by reacting alkenyl succinic anhydride, e.g. polyisobutenyl succinic anhydride, and an amine described in US-A-3202678, 3154560, 3172892, 3024195, 3024237, 3219666, 3216936 and BE-A-662875.

Alternatively the ashless dispersants may be esters derived from long chain hydrocarbon substituted carboxylic acids and from hydroxy compounds such as monohydric and polyhydric alcohols or aromatic compounds such as phenols and naphthols as prepared for example in US-A-3522179.

Hydroxyamines which can be reacted with any of the aforesaid long chain hydrocarbon substituted carboxylic acids to form dispersants include 2-amino-1-butanol, 2-amino-2-methyl-1-propanol, p-(beta-hy-

droxyethyl)-aniline, 2-amino-1-propanol, 3-amino-1-propanol, 2-amino-2-methyl-1 3-propane-diol, 2-amino-2-ethyl-1, 3-propanediol, N-(beta-hydroxy-propyl)-N'-(beta-aminoethyl)-piperazine, tris(hydroxmethyl) amino-methane (also known as trismethylolaminomethane), 2-amino-1-butanol, ethanolamine, beta-(beta-hydrox-yethoxy)-ethylamine, and the like. Mixtures of these or similar amines can also be employed.

Preferred dispersants are those derived from polyisobutenyl succinic anhydride and polyethylene amines, e.g. tetraethylene pentamine, polyoxyethylene and polyoxypropylene amines, e.g. polyoxypropylene diamine, trismethylolaminomethane and pentaerythritol, and combinations thereof. One particularly preferred dispersant combination involves a combination of (A) polyisobutenyl succinic anhydride with (B) a hydroxy compound, e.g. pentaerythritol, (C) a polyoxyalkylene polyamine, e.g. polyoxypropylene diamine, and (D) a polyalkylene polyamine, e.g. polyethylene diamine and tetraethylene pentamine using about 0.01 to about 4 equivalents of (B) and (D) and about 0.01 to about 2 equivalents of (C) per equivalent of (A) as described in US-A-3894763. Another preferred dispersant combination involves the combination of (A) polyisobutenyl succinic anhydride with (B) a polyalkylene polyamine, e.g. tetraethylene pentamine, and (C) a polyhydric alcohol or polyhydroxy-substituted aliphatic primary amine, e.g. pentaerythritol or trismethylolaminomethane as described in US-A-3632511.

The alkenyl succinic polyamine type dispersants can be further modified with a boron compound such as boron oxide, boron halides, boron acids and ester of boron acids in an amount to provide 0.1 to 10 atomic proportions of boron per mole of the acylated nitrogen compound as generally taught in US-A-3087936 and 3254025. Mixtures of dispersants can also be used such as those described in US-A-4113639.

The oils may contain from 1.0 to 10 wt %, more preferably 2.0 to 7.0 wt % of these dispersants.

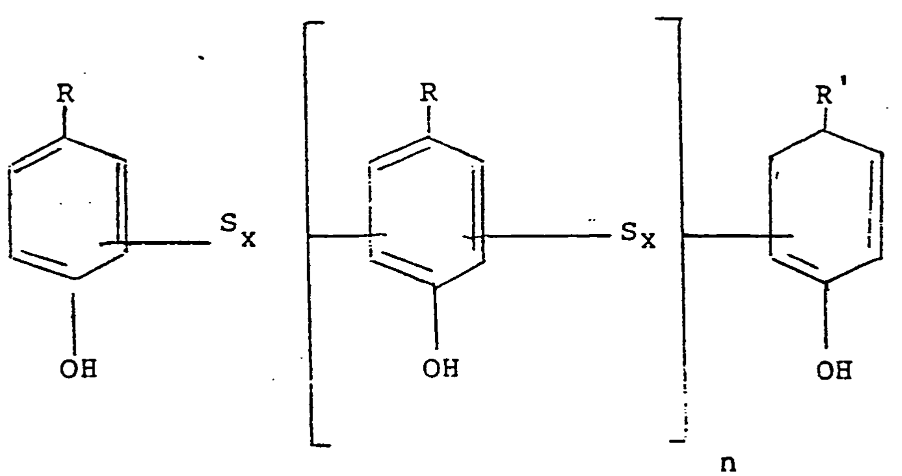
The dispersancy may be provided by 0.3 to 10% of a polymeric Viscosity Index imprever dispersant, for example copolymers of alkyl methacrylates with N-vinyl pyrrolidone or dimethylaminoalkyl methacrylate, alkyl fumarate-vinyl acetate N-vinyl pyrolidine copolymers, post-grafted interpolymers of ethylene-propylene with an active monomer such as maleic anhydride which may be further reacted with an alcohol or an alkylene polyamine, such as in US-A-4149984; or styrene/maleic anhydride polymers post-reacted with alcohols and amines, ethoxylated derivatives of acrylate polymers such as in US-A-3702300.

Magnesium and/or calcium containing additives are frequently included in lubricating compositions either alone or in combination with other alkali metal or alkaline earth metal additives such as those containing sodium. These may be present for example as the metal salts of sulphonic acids, alkyl phenols, sulphurised alkyl phenols, alkyl salicylates, naphthenates, and other oil soluble mono- and di-carboxylic acids.

Highly basic alkaline earth metal alkaryl sulfonates are generally known for example in US-A-3150088 and 3150089. For the purposes of this invention, a preferred alkaline earth sulfonate is magnesium alkyl aromatic sulfonate having a total base number (TBN, as measured by the procedure of ASTM D2896) ranging from 300 to 400.

Polyvalent metal alkyl salicylate and naphthenate materials may also be included, such as the methylene and sulfur bridged materials which are readily derived from alkyl substituted salicylic or naphthenic acids or mixtures of either or both with alkyl substituted phenols. Basic sulfurized salicylates and a method for their preparation are shown in US-A-3595791.

The sulfurized metal phenates can be considered the "metal salt of a phenol sulfide" which thus refers to a metal salt, whether neutral or basic, of a compound typified by the general formula:



where x = 1 or 2, n = 0, 1 or 2

or a polymeric form of such a compound, where R is an alkyl radical, n and x are each integers from 1 to 4, and the average number of carbon atoms in all of the R groups is at least about 9 in order to ensure adequate solubility in oil. The individual R groups may each contain from 5 to 40, preferably 8 to 20, carbon atoms. The metal salt is prepared by reacting an alkyl phenol sulfide with a sufficient quantity of metal containing material

to impart the desired alkalinity to the sulfurized metal phenate.

The sulfurized alkyl phenol is converted by reaction with a metal containing material including oxides, hydroxides and complexes in an amount sufficient to neutralize said phenol and, if desired, to overbase the product to a desired alkalinity by procedures well known in the art. Preferred is a process of neutralization utilizing a solution of metal in a glycol ether.

Magnesium and calcium containing additives such as described above although beneficial in other respects can increase the tendency of the lubricating oil to oxidise. This is especially true of the highly basic sulphonates.

According to a preferred embodiment the invention therefore provides a crankcase lubricating composition also containing from 2 to 8000 parts per million of calcium and/or magnesium.

The magnesium and/or calcium is generally present as basic or neutral detergents such as the sulphonates and phenates, and preferred additives are basic magnesium or calcium sulphonates. Preferably the oils contain from 500 to 5000 parts per million of calcium and/or magnesium from such additives.

These compositions of our invention may as an alternative or in addition contain other similar metal-containing detergent additives, for example, those containing barium, sodium, potassium or lithium.

The lubricating oil used in the lubricant composition may be a mineral lubricating oil or a synthetic lubricating oil or a mixture thereof. Suitable synthetic oils include diester oils such as di(2-ethyl-hexyl) sebacate, azelate and adipate; complex ester oils such as those formed for dicarboxylic acids, glycols and either monobasic acids or monohydric alcohols; silicone oils; sulfide esters; organic carbonates; hydrocarbon oils and other synthetic oils known to the art. The invention is particularly useful in mineral lubricating oils and has the added benefit that it may allow use of base stock oils that have inferior antioxidant properties to those currently used.

The lubricating compositions of the present invention may and usually will contain other traditional lubricant additives provided that they are substantially zinc-free and phosphorus-free - for example, rust inhibitors such as oleic acid and its derivatives such as N-oleylsarcosine, and oleic acid dimers and trimers, lecithin, sorbitan mono-oleate, dodecyl succinic anhydride or ethoxylated alkyl phenols; pour point depressants such as copolymers of vinyl acetate with fumaric acid esters of coconut oil alcohols; and viscosity index improvers such as olefin copolymers or polymethacrylates.

In copper-free oils other antioxidants in addition to the zinc dialkyldithiophosphate are sometimes required to improve the oxidative stability of the oil. These supplementary antioxidants are included especially when the basestock has poor oxidative stability; and typically the supplementary antioxidant is added to the oil in amounts from 0.1-1.5 wt %. The supplementary antioxidants that are used include phenols, hindered-phenols, bis-phenols, and sulphurised phenols, catechol, alkylated catechols and sulphurised alkyl catechols, diphenylamine and alkyl diphenylamines and phenyl-1-naphthylamine and its alkylated derivatives.

The inclusion of small amounts of copper generally removes the need for these supplementary antioxidants. It would, however, still be within the scope of our invention for a supplementary antioxidant to be included especially for oils operating under particularly severe conditions where the presence of such supplementary antioxidants may be beneficial, provided that substantially no phosphorus is thereby introduced.

Additives for lubricating oils are generally supplied as concentrates in oil for incorporation into the bulk lubricant. The present invention therefore provides concentrates comprising an oil solution containing: (1) less than 0.1 wt % of phosphorus and less than 0.1 wt% of zinc;

(2) from 1 to 50 wt % of an oil-soluble sulphur-containing compound;

(3) from 0.005 to 2 wt % of copper; and

(4) from 0.1 to 20 wt % of a bearing corrosion inhibitor,

and optionally a dispersant selected from the group consisting of:

(a) 0 to 60, e.g. 10 to 60 wt % of an ashless dispersant compound,

(b) 0 to 40, e.g. 3 to 40% of a polymeric viscosity index improver dispersant, although it is usual to add any viscosity index improver separately.

The concentrate may also contain other additives such as the detergents and viscosity index improvers previously described. A particularly preferred concentrate also contains a magnesium and/or calcium containing additive and the invention therefore provides a concentrate which further comprises from 0.1 to 8 wt % of calcium and/or magnesium.

The following Examples are now given, though only by way of illustration, to show certain aspects of the invention in more detail.

Comparative Examples I-VI and Examples 1 and 2

In the following Comparative Examples and Examples of the invention, formulations are prepared with the combinations and amounts of additives set out in Table 1, with the balance being a diluent oil suitable for lubricating compositions and comprising 0.3 wt % sulphur. The additives used are as follows:

A is a dispersant V.I. additive comprising an oil solution containing 21% of a multifunctional ethylene-propylene copolymer and containing 0.29 wt % N.

B is an ashless dispersant comprising a 50 wt % oil solution of borated polyisobutenyl succinimide having a polyisobutenyl radical with a molecular weight of approximately 950 and containing 1.6 wt % N and 0.35 wt % B.

C is an oil solution of an overbased magnesium sulphonate having a TBN of 400 and a magnesium content of 9.2 wt % and a sulphur content of 1.7 wt %.

D is an oil solution of an overbased calcium sulphonate having a TBN of 300 and a calcium content of 11.9 wt % and a sulphur content of 1.9 wt %

E is an oil solution of copper oleate containing 4 wt % copper.

F is a 30 wt % solution in oil of a hindered methylene bis-phenol antioxidant.

G is an alkylated diphenylamine antioxidant, commercially available as Irganox L-57 from Ciba-Geigy.

H is a 50 wt % oil solution of a zinc diamyl dithiocarbamate containing 6 wt % of zinc and 12 wt % sulphur.

J is an orthoborate ester made from ethoxyethanol comprising 5 to 6 wt % of boron.

K is 2,5-bis(nonyldithio)-1,3,4-thiadiazole, commercially available as Amoco 158 from Amoco Chemical Company, comprising 33 wt % sulphur.

L is an oil solution containing 12 wt % of molybdenum as the octoate.

M is a sulphurized ester sperm oil substitute, commercially available as Emery 9844 from Emery Corporation, and comprising 11.5 wt % sulphur.

The formulations were tested in the following standard tests:

Seq. IIID engine test according to ASTM STP 315M Part II in which the maximum and average cam plus lifter wear are measured. A pass in this test is achieved with maximum wear of 0.02 cm (0.008 in.) or better, and an average wear of 0.01 cm (0.004 in.) or better.

Kinematic viscosity increase in the IIID was measured at 40°C as a percentage increase in 64 hours. A pass is achieved in this test by achieving a viscosity increase in 64 hours of not more than 375%.

CRC-L-38 Screener engine test based on ASTM STP 509A PE IV in which the bearing weight loss (BWL) is measured. A pass in this test is achieved with BWL of not more than 40 mg.

The results are shown in Table 2. These results show the invention provides a surprising advantage in lubricants which have excellent antioxidant, anti-wear, and bearing corrosion inhibition with substantial absence of phosphorus and zinc. Comparative Examples I, II, and III show that in the absence of a bearing corrosion inhibitor, wear performance was inadequate. Comparative Example IV shows that the addition of a molybdenum additive did not improve wear performance. Comparative Example V shows that in the absence of copper antioxidant performance was inadequate even with conventional amounts of other known antioxidants.

The Examples of the invention show that the performance of the formulations is not merely summation of the performance of individual additive, but gives a surprising improvement in antiwear, antioxidant and bearing corrosion performance, while having phosphorus levels below those commercially employed in conventional oils.

Table 1

Example:	I	II	III	IV	V	VI	1	2
Additives (wt %)								
A	8.5	8.5	8.5	8.5	8.5	8.5	8.5	8.5
B	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
C	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
D	-	-	-	-	-	0.9	-	-
E	0.3	0.3	0.3	0.15	-	0.3	0.3	0.3
F	-	-	-	-	1.0	1.0	-	-
G	-	-	-	-	0.4	0.4	-	-
H	1.5	2.0	1.0	1.5	1.5	1.5	-	
J	-	-	-	-	1.0		1.0	-
K	-	-	-	-	-		-	0.5
L	-	-	-	0.03	-			-
M	-	-	-	-	-		3.0	3.0
Added Sulphur content (%)	0.51	0.57	0.45	0.51	0.51	0.53	0.67	0.84
Copper content (%)	0.012	0.012	0.012	0.006	0	0.012	0.012	0.012
Zinc content (%)	0.09	0.12	0.06	0.09	0.09	0.09	0	0
Phosphorus content (%)	0	0	0	0	0	0	0	0
Boron content (%)	0.01	0.01	0.01	0.01	0.06	0.01	0.06	0.01
Mg(Ca) (%)	0.15	0.15	0.15	0.15	0.15	0.15 (0.11)	0.15	0.15

Table 2

Example	I	II	III	IV	V	VI	1	2
Seq. IIID max. wear (cm)	0.027 F	0.0546 F	F*	0.0290 F	0.028 P	0.33 F	0.0056 P	0.0013 P
ave. wear (cm)	0.012 F	0.0236 F	F*	0.0163 F	0.0015 P	0.02 F	0.0023 P	0.0008 P
Viscosity inc. (%) at 64 hours	102 P	66 P	*	104 P	400 +/48 hr F	65 P	-	67 P
CRC-L-38 BWL (mg)	-	88.3 F	-	-	-	5 P	-	3.3 P

P = Pass

F = Fail

* = Test not completed, failure after 4 hours.

- = Not tested.

Concentrates - Typical concentrates for providing the above formulations.

	Component	wt %	%S	%Cu	%B
Example 1	B	33.7			0.12
	C	18.0	0.31		
	E	3.4		0.16	
	J	11.2			0.56
	M	33.7	3.88		
		100.0	4.19	0.16	0.68
Example 2	B	35.7			
	C	19.1	0.32		0.13
	E	3.6		0.14	
	K	5.9	1.95		
	M	35.7	4.09		
		100.0	6.36	0.14	0.13

Concentrates may also contain some dilute oil to improve handling (reduce viscosity).

Claims

1. A crankcase lubricant composition for use in automobile engines comprising a major amount of a lubricating oil, 5 to 500 parts per million by weight (ppm) of added copper present in oil-soluble form, one or more added oil-soluble sulphur-containing compounds such that the composition comprises from greater than 0.5 to 2.0 wt % of total sulphur and an effective amount of a bearing corrosion inhibitor, the composition containing less than 0.05 wt % phosphorus and less than 0.01 wt% zinc.

2. A composition as claimed in claim 1, in which the amount of added copper in the composition is from 10 to 400 ppm.

3. A composition as claimed in claim 2, in which the amount of added copper in the composition is from 10 to 200 ppm.

4. A composition as claimed in claim 3, in which the amount of added copper in the composition is from 60 to 200 ppm.

5. A composition as claimed in any of the preceding claims, in which copper may be blended into the oil as the copper salt of a C_{10} to C_{18} fatty acid, an unsaturated carboxylic acid, a naphthenic acid of molecular weight from 200 to 500 or an alkyl or alkenyl substituted dicarboxylic acid, an oil-soluble copper dithiocarbamates of the general formula $(RR'NCSS)_nCu$, where n is 1 or 2 and R and R′ are the same or different hydrocarbyl radicals containing 1 to 18 carbon atoms, a copper sulphonate, a copper phenate, or a copper acetylacetonate.

6. A composition as claimed in any of the preceding claims, in which the oil-soluble sulphur compound is a dithiocarbamate of the formula: $(RR'NCSS)_n$ M (wherein R, R′ and n are as defined in claim 5 and M is a suitable metal) or a mercaptide, a sulphurized unsaturated organic compound, a sulphide, a thioether, a thiophenol, a thioxanthate, a sulphurized ester, a thioester, a thioamide, a thiazole or a thiadiazole.

7. A composition as claimed in claim 6, in which the oil-soluble sulphur compound is a dialkyl dithiocarbamate containing 2 to 12 carbon atoms.

8. A composition as claimed in any of the preceding claims, which contains from greater than 0.5 to 1.0 wt % total S, including from 0.1 to 0.5 wt % S as added oil-soluble sulphur-containing compound.

9. A composition as claimed in any of the preceding claims, which is substantially zinc-free.

10. A composition as claimed in claim 6 which contains from 0.5 to 3 wt % sulphurized ester.

11. A composition as claimed in any of the preceding claims, in which the bearing corrosion inhibitor comprises one or more borate esters of the formula:

$B(OR)_3$ or $(RO)_2B\text{-}O\text{-}B(OR)_2$, $(ROBO)_3$ or $(RO)_2BO\text{-}R^1\text{-}OB(OR)_2$

(wherein R is a substituted or unsubstituted alkyl, aryl or aralkyl group or two groups R together form a substituted or unsubstituted alkylene group and R^1 is a substituted or unsubstituted alkylene group) and/or a thiadiazole polysulphide containing from 5 to 50 carbon atoms, a derivative or polymer thereof.

12. A composition as claimed in claim 11, which contains from 0.01 to 10 wt % of a borate ester.

13. A composition as claimed in claim 11 or claim 12, in which the borate ester is a tris(ethoxyethyl) orthoborate ester or a biborate of butane-1,3-diol.

14. A composition as claimed in claim 11 which contains from 0.01 to 10 wt % of 2,5-bis(t-nonyldithio)-1,3,4-thiadiazole.

15. A composition as claimed in any of the preceding claims, which contains less than 0.005 wt % of phosphorus.

16. A composition as claimed in claim 15 which is substantially free of phosphorus.

17. A composition as claimed in any of the preceding claims, which further comprises:

(A) from 1 to 10 wt % of an ashless dispersant compound and/or

(B) from 0.3 to 10 wt %, of a nitrogen or ester containing polymeric viscosity index improver dispersant.

18. A composition as claimed in any of the preceding claims, which comprises from 2 to 8000 parts per million of calcium and/or magnesium.

19. A composition as claimed in claim 18, which comprises from 500 to 5000 parts per million of calcium and/or magnesium as a basic calcium and/or magnesium sulphonate.

20. A composition as claimed in any of the preceding claims, which further comprises one or more of rust inhibitors, pour point depressants, additional anti-oxidants and viscosity index improvers.

21. A concentrate comprising an oil solution containing:

(1) less than 0.1 wt % of phosphorus; and less than 0.1 wt % of zinc;

(2) from 1 to 50 wt % of an oil-soluble sulphur-containing compound;

(3) from 0.005 to 2 wt % of copper;

(4) from 0.1 to 20 wt % of a bearing corrosion inhibitor; and

(5) from 0 to 60 wt % of an ashless dispersant and/or from 0 to 40 wt % of a polymeric viscosity index improver dispersant.

22. A concentrate as claimed in claim 21, which further comprises from 0.01 to 8 wt % of calcium and/or magnesium.

23. The use of oil-soluble copper as antioxidant in a zinc-free and phosphorus-free lubricant composition comprising an oil-soluble sulphur-containing compound, a bearing corrosion inhibitor, and ashless dispersant and/or a polymeric viscosity index improver dispersant, and a calcium and/or magnesium containing detergent.

24. The use in a crankcase lubricant composition for automobile engines which contains less than 0.05 wt % phosphorus and less than 0.01 wt % zinc, of 5 to 500 ppm of added copper present in an oil-soluble form, from greater than 0.5 to 2.0 wt % of total sulphur, and a bearing corrosion inhibitor to control oxidation, wear and corrosion and meet at least the quality standard of category SF and/or CD of the API Engine Service Categories.